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INFLUENCE OF ADSORPTION PHENOMENA ON OXIDATION
OF METALS AT HIGH TEMPERATURES

[Comment: This report presents the full text of an article by Dipl. Chem. H. W. Engell and Prof Dr Engr K. Hauffe, submitted from the Institute of Physical Chemistry of the University of Greifswald, and published in Metall, Volume 6, 1952, No 11/12, pages 285-291, Berlin.

Numbers in parentheses refer to appended authors' bibliography.]

Statement of the Problem

In spite of the simple equation for the chemical reaction

$$metal + oxygen = metal\text{-}oxide$$
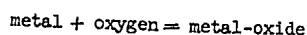
the oxidation of metals has a rather complicated reaction mechanism since the reaction product, the metal-oxide, separates the two reactants from one another. Thus, the total oxidation process comprises the two phase boundary reactions at the phase boundaries metal/metal-oxide and metal-oxide/oxygen and the diffusion of ions and electrons through the metal-oxide layer as depicted in Figure 1.
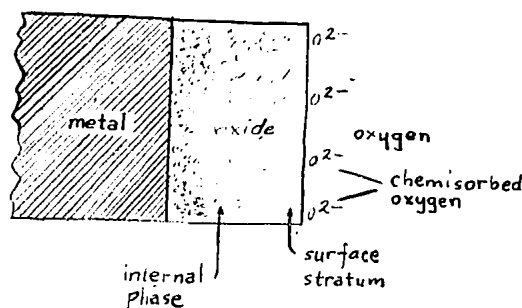

Figure 1. Schematic Representation of the Density of the Quasi-Free Electrons in the Oxide Layer of a Scale System Metal/Metal-Oxide/Oxygen

In the last few decades, a large amount of theoretical and experimental research has been published to explain these component processes and to clarify their effect on the total course of the oxidation. As a result, today we are in a position to decide clearly whether diffusion phenomena in the oxide layer or phase boundary reactions are rate-determining. Although in the case of the formation of solid porefree surface layers the parabolic oxidation law of Tamann (1) is valid, in the case of porous surface layers the phase boundary reactions are slowest and are therefore the rate-determining reactions because here the oxygen passes quickly enough through the pores of the surface layer to the metal.

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For the following discussion, however, we wish to consider the formation of porefree oxide layers only. Under these conditions the diffusion phenomena of the starting materials, either the metal or metalloid, are usually rate-determining. According to a hypothesis by Wagner (2), atoms do not diffuse through the oxide or scale layer; only ions and electrons do so. Furthermore, Wagner was able to show that a migration of ions or electrons can take place in the scale layers only through the lattice vacancies. (There are ions in the interstices and ionic lattice vacancies or quasi-free electrons and elec-tron-defect places.) By extending the Wagner-Schottky Lattice Vacancy Theory (3), Wagner was able to develop, by means of the general formula, a theory of the oxidation of a metal of which the oxidation rate can be calculated from the free energy of the oxidation, from the electrical capacity and the trans-fer numbers of the ions and electrons, or from the free energy of the oxidation and the autodiffusion coefficients of the ions participating in the diffusion through the scale layer. By extension of these relationships and application of the lattice-vacancy theory extended to heterotypical mixed phases (5), Wagner (6), as well as Hauffe and his collaborator (7), applied the Theory of Oxida-tion Phenomena to metal alloys.

While more has become recently known about oxidation reactions with rate-determining diffusion phenomena, the participation of phase boundary reactions has had only limited consideration. Judging from available experimental obser-vations, in most cases with fast diffusion phenomena, the phase boundary is the rate-determining component of the oxidation. Thus, the dissociation rate of the oxygen molecule or an established adsorption equilibrium can be considered of importance. However, this by no means exhausts the possibilities of the phase boundary reaction.

In analogy to the surface layer theory of the crystall rectifier of Schottky and Spenke (8), Hauffe and Engell (9) have been able to show that, for the chemisorption of oxygen on a metal-oxide, a surface layer of the oxide of up to 1,000 angstroms is added to the phase boundary; this will be discussed in more detail below. The phase boundary metal-oxide/oxygen is, first, the place at which the adsorption of gaseous oxygen and the subsequent formation of oxygen ions take place, i.e., the chemisorption. As indicated elsewhere, the surface stratum of the oxide plays a critical role. (9, 10) Because of the importance of the participation of the surface stratum to oxida-tion phenomena, which can lead to experimental findings that cannot be inter-preted directly in terms of present knowledge, we wish to deal in this paper especially with such phase boundary reactions.

Moreover, in dealing with reactions on the phase boundary metal/metal oxide, the existence of a surface stratum will have to be considered, and in this case assumptions based on the Theory of Crystal Rectifiers will be promising.

Adsorption and Phase Boundary Reactions

Recently, Hauffe and Pfeiffer (11) referred to the fact that the oxidation rate of iron at fixed temperatures in CO-CO_2 mixtures is determined by phase boundary reactions. To some degree the experiments can be interpreted by means of plausible assumptions concerning the chemisorption of the CO_2 on the FeO scale layer.

Earlier, Moore and Lee (12) attempted to interpret their oxidation research on zinc in a similar manner. Their experiments showed a clear relationship of the oxygen pressure to the oxidation rate that is inexplainable in the Wagner Scale Theory. (2, 4) Also, Moore and Lee assumed, in the interpretation of their experiments, that the chemisorption of the oxygen on the ZnO of the sur-face layer was the rate-determining factor. Of course, they found a parabolic

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function that was not consistent with the first assumption. How both circumstances (oxygen pressure relation ... p to the oxidation rate and the parabolic time functions) can be interpreted at the same time from the adsorption properties of the ZnO layer will be shown below after discussion of the general concepts. Furthermore, Vernon and coworkers (13) were able to show that the oxidation rate of zinc, especially at lower temperatures between 190 and $300^{\circ}C$, can be described by a logarithmic time function, which can also indicate phase boundary phenomena.

It is thus understandable that the problem of adsorption on scale layers has been of great interest. Also the following observation is of interest in this connection: If an iron sheet is heated in high vacuum (p_{O_2} about 10^{-6} to 10^{-4} Torr) at $1,000^{\circ}C$, there is no measurable weight increase of the sample even after several hours. If, on the other hand, the sample is placed in a $CO-CO_2$ mixture that has a very low oxygen partial pressure ($p_{O_2} < 10^{-10}$ Torr), then at the same temperature after several hours the sample will be completely oxidized. (11) The oxidation rate under the experimental conditions is proportional to the quotient $(p_{CO_2}/p_{CO})^{2/3}$. As the cause of this phenomena, we might assume a specific adsorption of CO_2, which in this case acts as the oxidizing agent, on the iron oxide surface layer. Molecular oxygen, on the other hand, is evidently adsorbed much less strongly and therefore effects an oxidation rate that is much slower at these low pressures.

In the following discussion, the "chemisorption" (activated adsorption activated by chemical forces between the surface layer of the adsorbent and the adsorbate) of oxygen on oxide layers will be considered. Essentially, we shall bring the same concepts into use that we developed i~ ~r lecture at the meeting of the Deutsche Bunsengesellschaft in Berlin in January 1952 (9) and in another place with W. Schottky (10).

The influence of chemisorption on scale phenomena can be quite variable. A possibility of this influence has already been briefly indicated for the example of the oxidation of iron in a $CO-CO_2$ mixture. After discussing the general mathematical interrelationships of chemisorption and then several special aspects of the relationship between lattice vacancy phenomena in oxide surface layers and chemisorption, we will consider the influence of chemisorption on the mechanism governing the formation of "thick" scale layers (layer thickness $> 10^{-4}$ cm). According to current theoretical developments (9), an influence of chemisorption is to be expected on the growth of such layers if the chemisorption itself or subsequent reactions at the phase boundary oxide/oxygen are rate-determining. Furthermore, it is evident what influence the alloying materials can exert in this case.

Next, we will consider the relationship between chemisorption and the formation of "thin" surface layers (10^{-6} to 10^{-5} cm). In this case, the chemisorption controls the kinetics of the tarnish phenomena if the transfer processes in the surface layer are rate-determining. The question whether phase boundary reactions or transfer processes are rate-determining can be answered from the form of the tarnish function according to the following aspects:

1. A parabolic time function points in all cases to the fact that transfer processes are rate-determining (Tammann Tarnish Law). If an electron-defect conducting surface layer is formed, the parabolic tarnish constant is completely dependent on the oxygen pressure. (2, 4,) If the surface layer is an excess conductor, then the tarnish constant is a function of the oxygen pressure only with "thin" surface layers.

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2. A linear time function always means that the phase boundary reactions are rate-determining. In this case, we are dealing with a reaction at the oxide/oxygen boundary; thus the tarnish constant depends on the oxygen pressure. Of course, with defect-conducting oxide layers, the rate of the phase boundary reactions at the metal/metal-oxide boundary can also be dependent on the oxygen pressure so that a clear conclusion concerning the reaction mechanism in the case of a linear time function is possible only for metals whose oxides are electron-excess conductors.

Finally, these considerations will be applied to the oxidation of zinc (according to the measurements of Moore and Lee), and it will be shown that theory and experimental data are in good agreement.

Adsorption and Outer Layer Formation

For the following discussion, we assume that an oxide layer on a metal or alloy is more than 1,000 angstroms thick and that the growth of this layer continues. In the case of an electron-excess conducting surface layer, the mass transfer from the metal to the boundary oxide/oxygen is effected by cations in the interstitial positions or oxygen ion lattice vacancies, which are formed continually at the metal/metal-oxide boundary and combine with the chemisorbed oxygen to form the metal-oxide at the oxide/oxygen boundary. The entire process might take place in the following steps:

1. Solution of the metal in the oxide with dissociation of the dissolved metal atoms into interstitial position cations $MeO^{\cdot\cdot}$ and quasi-free electrons
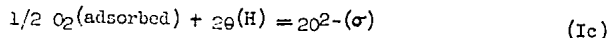
$$Me = MeO^{\cdot\cdot} + 2\theta(H) \tag{Ia}$$

The index H signifies here and in the following discussion a particle in the semiconductor interior; therefore, in the internal phase of the surface layer.

2. Adsorption of oxygen on the oxide:

$$O_2(g) = O_2(adsorbed) \tag{Ib}$$

3. The chemisorption of the oxygen with the consumption of the quasi-free electrons of the oxide layer:

$$1/2\ O_2(adsorbed) + 2\theta(H) = 2O^{2-}(\sigma) \tag{Ic}$$

The symbol $O^{2-}(\sigma)$ will represent a chemisorbed oxygen ion to which two electrons of the ZnO are attached, either because a surface bonding (covalent or ionic) is formed between oxygen and oxide, or in the manner suggested by Weyl (14) by polarization of the conductivity bond of the oxide through the oxygen of the surface layer. An $O^{2-}(\sigma)$ forms, therefore, two "surface charges." Figure 2 illustrates the energy relationship on the oxide/oxygen boundary which initiates process (Ic).

4. Formation of a new lattice plane of metal-oxide by reaction between chemisorbed oxygen and interstitial cations which migrate by diffusion or other transfer means to the oxide/oxygen boundary:

$$MeO^{\cdot\cdot} + O^{2-}(\sigma) \rightleftharpoons MeO \tag{Id}$$

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With the transfer of quasi-free electrons and interstitial cations that have been formed in the vicinity of the metal/metal-oxide boundary by dissociation of the metal atoms dissolved in the oxide, at the oxygen/metal-oxide boundary the electrons are attracted to the cations on the basis of their greater mobility; however, the spatial separation of the positive and negative charges in the interior of the oxide layer ("internal phase") with adequate electron concentration and layer thickness is so unimportant that a quasi-neutrality can be assumed.

The charge distribution in the vicinity of the oxide/oxygen boundary behaves otherwise. By the transfer of quasi-free electrons in surface charges through the chemisorption of oxygen at the surface, an electron-repelling surface field results and thereby there is a decrease in negative charges within the surface stratum of the oxide and hence the formation of a positive space charge is sponsored (9) (see Figure 1). The process is analogous to the formation of surface strata of crystal rectifiers and permits us to deal formally in the same manner as Schottky and Spenke (8) have dealt with these surface strata (Figure 3).
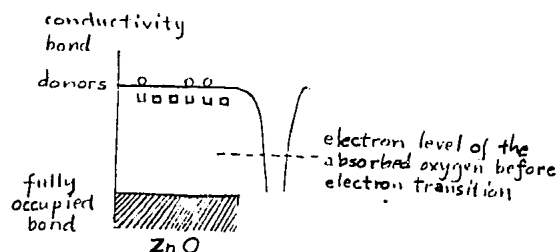

Figure 2. Simplified Energy Diagram for the Adsorption of Oxygen on ZnO Before the Electron Transfer From the Conductivity Bond
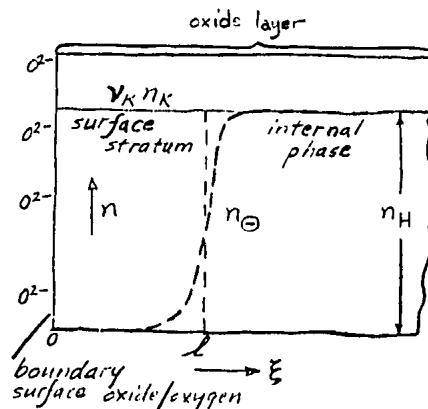
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Figure 3. Simplified Representation of the Charge in Concentration of Quasi-Free Electrons n_Θ and the Metal Ions in the Interstitial Position n_k in the Internal Phase ($1/2 n_k = n_\Theta = n_H$) and in the Surface Stratum

The surface stratum formation and chemisorption are controlled reciprocally and both are affected by the type and concentration of the lattice vacancies in the oxide. It is therefore possible to make predictions from the lattice vacancy situation in the internal phase of the oxide layer concerning the adsorption behavior of the layer that is of great importance in the clarification and effect of the tarnish phenomena if the phase boundary reactions are rate-determining.

Influence of the Space Charge in the Surface Stratum on the Transfer of Cations Through the Oxide Layer

As mentioned at the outset, the progress of the oxidation is made possible, according to Wagner (2), by the fact that the metal ions and the electrons are transferred through the oxide layer to the metal-oxide/oxygen boundary. This transfer can result both from diffusion and migration in the electrical field so that in general the following function is valid.

$$s_\Theta = D_\Theta \frac{\partial n_\Theta}{\partial \xi} - \mathcal{E}(\xi) \cdot n_\Theta \cdot B_\Theta \tag{IIa}$$

$$s_K = D_K \frac{\partial n_K}{\partial \xi} + \gamma_K \mathcal{E}(\xi) \cdot n_K \cdot B_K \tag{IIb}$$

These relationships must be fulfilled at each position of the semiconductor. In these equations, S designates the stream (i.e., the number of electrons or cations which arrive per second on a sq cm of the outer surface) of cations or electrons toward the outer surfaces; D is the diffusion coefficient in cm²/sec; B is the mobility in cm²/volt·sec; ξ is the position coordinate directed from the gas/oxide boundary toward the interior; and $\mathcal{E}(\xi)$ is the field strength in volt/cm at position ξ. Furthermore, n_k and n_Θ mean the concentration of the metal ions in the interstitial positions and the quasi-free electrons; and γ_K is the charge of the cations in the interstices. The concentration distribution of the positive and negative charges in the surface stratum is defined by these conditions, as well as by the following equations from the Boltzmann function:

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$$\frac{n_R}{n_H} = \exp\left(-\frac{V_D}{\mathcal{D}}\right) \qquad\qquad\text{(III)}$$

Here n_R is the concentration of the quasi-free electrons in the surface stratum; n_H is the same in the internal phase of the surface layer; V_D is the diffusion potential between the internal phase and the surface based on the space charge in the surface stratum of the surface layer; and $\mathcal{D} = kT/e$.

Under the action of the space charge in the surface stratum, the migration of the lattice interstitial cations to the oxide/oxygen boundary is accelerated. To the diffusion, according to the first term of the sum of equation II, is added a field current represented in equation II by the second term. Thus there is a reduction in the concentration of positive charges of the surface stratum and consequently a reduction of the field strength $\mathcal{E}(\xi)$ in the surface stratum and of the diffusion potential V_D and thereby again a reduction in field current. A stationary position is reached when the concentration distribution of the interstitial cations in the surface stratum are so oriented that a divergence-free stream of cations flows through the entire surface layer (surface stratum and internal phase). In the internal phase, the forward flow of the electrons ahead of the cations brings about a diffusion energy that is in addition to the drop in concentration. This type of mass transfer is called ambipolar diffusion. For the stream of the interstitial cations, it is true that in this case of ambipolar diffusion in the internal phase we have, using $D_K = B_K B$,

$$S_K = (1+\nu_K)\,\mathcal{D}\cdot B_K\cdot\frac{\partial n_K}{\partial \xi} \quad \text{for } \xi \geq \ell \qquad\qquad\text{(IIc)}$$

In the surface stratum, the diffusion component compared with the field component is to be disregarded, so that from equations IIb and IIc we can write for the stationary divergence-free cation current through the total surface layer the postulate

$$\left\{(1+\nu_K)\,\mathcal{D}\cdot B_K\cdot\frac{\partial n_K}{\partial \xi}\right\}_{\xi\geq 1} = \left\{\nu_K\cdot n_K(\xi)\cdot B_K\cdot\mathcal{E}(\xi)\right\}_{\xi< \ell} \qquad\qquad\text{(IIb)}$$

Here the left member of the equation is based on the particle flow in the internal phase; the right, on the particle flow through the surface stratum. By introducing the Poisson equation

$$\frac{\partial \mathcal{E}}{\partial \xi} = \frac{4\pi e}{\varepsilon}\cdot\nu_K\cdot n_K(\xi) \quad -$$

(ε = the dielectric constant) and integrating from $\xi = 0$ to $\xi = \ell$, we find that for the concentration of the cations in the interstitial position at point ξ of the surface stratum

$$n_K(\xi) = \left\{\frac{\varepsilon}{8\pi e}\cdot\frac{(1+\nu_K)}{\nu_K^2}\cdot\mathcal{D}\cdot\left(\frac{\partial n_K}{\partial \xi}\right)\right\}_{\xi\geq \ell}^{1/2}\cdot(\ell-\xi)^{-1/2}. \qquad\qquad\text{(IV)}$$

The thickness of the surface stratum is obtained by repeated integration between the limits 0 and ℓ

$$\ell = \left(\frac{3}{2}\right)^{2/3}\cdot\left(\frac{\varepsilon}{8\pi}\right)^{1/3}\left\{(1+\nu_K)\cdot\mathcal{D}\cdot\left(\frac{\partial n_K}{\partial \xi}\right)_{\xi\geq \ell}\right\}^{-1/3}\cdot V_D^{2/3}. \qquad\qquad\text{(V)}$$

In this derivation, as will be done throughout the following discussion, it is presumed that V_D represents the actual potential between the surface and the internal phase of the oxide layer. For a critical discussion of this assumption, see Engell, Hauffe, and Schottky. (10) Furthermore, equation IV is valid only for $\xi < \ell$ since $\xi = \ell$ gives $n_K(\xi) = \infty$, which naturally is not true. However, equation IV defines the curve of n_K up to just before the limit between

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the surface stratum and the internal phase. From equation V it is apparent that the surface stratum thickness l increases when the concentration drop of the cations in the internal phase

$$\left(\frac{\partial n_K}{\partial \xi}\right)_{\xi \geq l}$$

decreases. This finding results from the demand of a divergence-free cation flow through the entire surface layer and is clearly understandable: The growth of the surface stratum thickness causes a decrease of the cation flow through the surface stratum. In the internal phase, the cation flow likewise drops with $\left(\frac{\partial n_K}{\partial \xi}\right)_{\xi \geq l}$ and therefore, the right and left sides of equation IIb assume the same value.

Equations IV and V describe the concentration of the interstitial ions in the surface stratum and the surface stratum thickness during the steady course of the oxidation. V_D depends on the concentration of the chemisorbed oxygen ions on the surface of the scale layer and this in return is related to the lattice-vacancy concentration n_H and the oxygen pressure P_{O_2} through the equation:

$$n_{O^{2-}}^{(\sigma)} = 1/4 \left\{ \frac{E}{\pi e} \cdot n_H \cdot \ln \frac{P_{O_2}^{1/2} \cdot n_K^2 \cdot K}{n_{O^{2-}}^{(\sigma)}} \right\}^{1/2} \tag{VI}$$

The derivation of this formula is detailed by Engell, Hauffe, and Schottky. (10)

All the derived formulas are exactly valid only for so-called surface strata of discharge, the appearance of which is to be assumed in general at higher temperatures.

Influence of Surface Stratum Formation on the Formation of Thick Scale Layers

Concerning the kinetics of the growth of thick excess conducting oxide layers, the formation of the surface stratum at the oxide/oxygen boundary will be of influence when and only when phase boundary reactions, as already shown can be heterogeneous. We wish to consider thick an oxide layer the thickness of which is a multiple of the surface stratum thickness, i.e., in general thicker than 10^{-5} cm. If we assume, for simplification, that the rate-determining reaction at the oxide/oxygen boundary proceeds in proportion to the concentration of the chemisorbed oxygen, $n_{O^{2-}}^{(\sigma)}$, and thus from Equation VI it follows:

$$\sim n_{O^{2-}}^{(\sigma)} \sim n_H^{1/2} \quad \text{for } P_{O_2} = \text{const.} \tag{VII}$$

Now, there is the possibility that the concentration of the quasi-free electrons in the scale layer can be varied as when the basic metal is alloyed and the new ions have different valence than the basic metal. (5) With higher-valence ions the number of quasi-free electrons is increased, and with lower-valence additives the number of quasi-free electrons is decreased. From equation VII it can be seen that the oxidation rate also decreases with lower-valence additives and is increased by higher-valence additives, provided, as was assumed, that the react' 1 rate is proportional to the concentration of the chemisorbed oxygen on the oxide surface.

If, on the other hand, the transfer of the cations in the interstices through the oxide layer to the oxide/oxygen boundary is time-determining, then the influence of the alloying metals is counteracted. As Wagner (15) and Hauffe (16) have been able to show, the concentration of the interstitial cations is decreased by admixture of higher-valence cations to an excess

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conductor and increased by the addition of lower-valence cations, which result in a decrease in the oxidation rate in the first case and an increase in the second. For electron-defect conducting scale layers, the relationship is reversed; however, the influence of the adsorption on the oxidation rate is dealt with in a different manner.
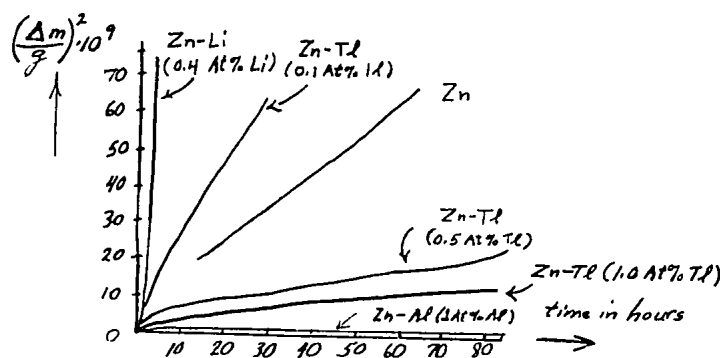

Figure 4. Time Curve of the Oxidation of Zinc Alloys in Air at 700°C According to Gensch and Hauffe

As an example of the effect of alloy additions on the oxidation of zinc scale which form excess conducting scale layers, in Figure 4 is plotted the oxidation rate of zinc alloys according to Gensch and Hauffe. (17) In effect, a parabolic time function is valid; with these experiments the boundary reactions were not rate-determining, but rather the transfer over the rate-determining. The curvature changes of the curves are with thickness of the scale layer, as will be discussed below.

The question of when diffusion and when phase boundary reactions of the element, and therefore the time-determining, component of the oxidation process cannot be unequivocally answered at present because of the numerous and different and a large number of various influences. However, it may be understood from the above discussion that in the case of base metals, higher-valence admixtures will favor transfer process as the rate-determining component, and lower-valence admixtures will favor adsorption or other phase boundary reactions as the determining factor. This is true only for metals which form an electron-excess conducting oxide.

Influence of the Adsorption and Interface on the Oxidation Rate with the Formation of Thin Oxide Layers

If phase boundary reactions are rate-determining, then with thin layers it is to be expected that the oxidation rate follows a linear time function ($d \xi / dt = $ ...), and also, in the case of excess-conducting scale layers, of on the oxygen pressure. (For defect-conducting scale layers, this is not true when the diffusion is time-determining.) However, if the thickness of the scale layer is smaller or of the same order as the surface stress ξ ("thin" scale), then it is to be reckoned that the oxidation rate

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on the oxygen pressure if the transfer of the metal ions from the metal through the scale to the oxide/oxygen boundary is time-determining, which will be shown in the following discussion. Simultaneously, however, a parabolic tarnish function will be found.

The formation of scale layers having this limited thickness has already been considered by Cabrera and Mott (18); however, these authors have not agreed on the relationship of the oxygen pressure to the oxidation rate. The type of treatment chosen by us differs from the treatment of Cabrera and Mott in several points; however, we obtained quite similar results. In the first stage of the oxidation when the thickness of the oxide layer ξ_1 has not yet reached the maximum value of the surface stratum ℓ, with constant surface stratum potential the decreasing field strength with the scale thickness will be $\mathcal{E}(\xi_1) > \mathcal{E}(\ell)$. In this case, the electrons that are formed by dissociation of the metal atoms dissolved in the oxide migrate almost completely to the adsorbed oxygen and appear as surface charges, because we now have to consider the oxide layer not only as the "surface stratum" but also as a growing surface stratum. With this limited scale thickness, moreover, an appreciable number of electrons can migrate to the surface by thermal emission or tunnel effect from the metal through the oxide. This number (n) we assume to be large compared with $n_H \cdot \xi_1$. Therefore, we consider the surface stratum a "vacant layer" since also with vacant layers the number of positive charges present in the surface stratum n_H can be neglected. In this case, a field strength independent of location of the order V_D / ξ_1 prevails in the surface stratum.
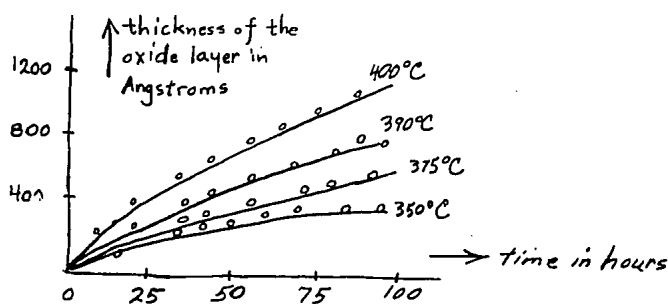

Figure 5. Time Function of Zinc Oxidation at 100-mm Mercury Pressure at Various Temperatures According to Moore and Lee
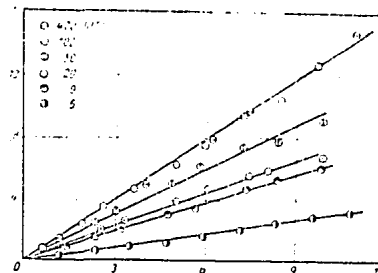
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Figure 6. Increase in Thickness of the TiO layer at Various Oxygen Pressures for 400°C According to the Parabolic Oxidation Function Plotted by Moore and Lee
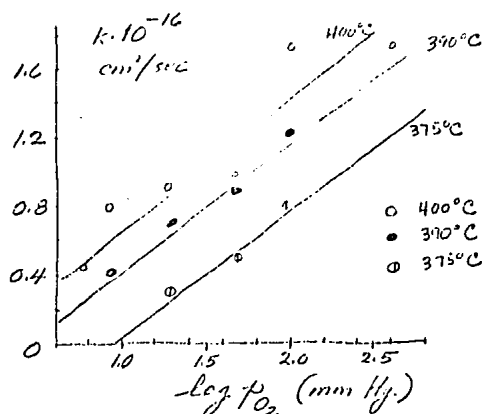

Figure 7. Logarithmic Curve of the Relationship of the Oxygen Pressure to the Parabolic Tarnish Constants k; Plotted According to the Oxidation Experiments of Moore and Lee

For the deviation of the tarnish function for the formation of thin excess-conducting oxide layers, we assume that a number n of electrons proceed from the metal into the oxide layer by thermal emission. The assumption of a tunneling (channeling) of electrons was not actually required by the findings. To arrive at the surface of the oxide and then to be able to react with oxygen, the electrons must back against the electrical field in the surface structure which originates from the already present adsorbed oxygen. Accordingly, we have (see the derivation of the analogous formula in Engell, Hauffe and Hilbrandt, loc. cit.):

$$\frac{n_{c2}^{(\sigma)}}{N+n_{02-}^{(\sigma)}} = K \cdot p_{O_2}^{1/2} \cdot n^2 \cdot \exp(-2\mathcal{E}(\xi_1) \cdot \frac{\xi_1}{\mathcal{D}}) \qquad \text{(VIII)}$$

Where N is the number of similar addition positions for a chemisorbed oxygen atom per sq cm of surface of the oxide and K is a constant. For low surface concentrations $(N \gg n_{02-}^{(\sigma)})$ we can write:

$$\mathcal{E}(\xi_1) = \frac{4\pi e}{\epsilon} \cdot 2n_{02-}^{(\sigma)} = K' \cdot p_{O_2}^{1/2} n^2 \cdot \exp(-2\mathcal{E}(\xi_1) \cdot \frac{\xi_1}{\mathcal{D}}) \qquad \text{(IX)}$$

$$\text{with } K' = K \frac{8\pi e}{\epsilon} \cdot N$$

and finally after modification

$$\mathcal{E}(\xi_1) \approx \frac{\mathcal{D}}{4\xi_1}\left\{ \ln(p_{02} \cdot n^4 K'^2) - 2\ln\mathcal{E}(\xi_1) \right\} \qquad \text{(X)}$$

In this expression $\ln\mathcal{E}(\xi_1)$ is negligible compared with $\mathcal{E}(\xi_1)$ because $\mathcal{E}(\xi_1)$ is of the order of 10^5 V/cm.

The transfer of cations from the metal to the oxide/oxygen boundary takes place according to equation IIb. If the field strength is great, then the diffusion current is negligible compared with the field current, and one obtains:

$$S_k = n_k \cdot B_k \cdot \mathcal{E}(\xi) \cdot \nu_K \qquad \text{(XI)}$$

From equations X and XI there follows as the final equation from the cation flow (i.e., the number of cations which arrive at the surface per second per sq cm)

$$S_K = n_K \cdot B_K \cdot \nu_K \cdot \frac{\mathcal{D}}{4\xi_1} \cdot \ln(p_{02} \cdot n^4 \cdot K'^2) \qquad \text{(XII)}$$

If the transfer of the cations to the surface is rate-determining for the oxidation of the metal, then equation XII leads to a time function of the form

$$\frac{d\xi}{dt} = \frac{A}{\xi}$$

$$\text{where } A = \frac{V_m}{N_L} \cdot B_K \cdot V_K \frac{\mathcal{D}}{4}\left\{ \ln p_{02} + \ln(n^4 K'^2) \right\}$$

(V_m = mol volume of the oxide; N_L = Loschmidt number.)

a parabolic tarnish function.

The field strength of the scale layer amounts to about 10^5 V/cm for layer thicknesses of about 1,000 angstroms. If the layers are too thick then the reaction comes to a halt if the temperature is not high enough for the diffusion to cause an adequate transfer of cations to the surface. This stoppage of the growth or transition to another time function will result from thinner scale layers the lower the oxygen pressure and the lower the temperature because according to equation X in both of these cases $\mathcal{E}(\xi_1)$ and thereby the field current of the cations decreases.

The oxygen pressure dependence of the rate constants of the parabolic tarnish function XIII follows from equation XII

$$A = A_0 \cdot \ln p_{02} + \text{const.}$$

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The slope of the curves in Figure 4 with small layer thickness may be such that first equations XII and XIII determine the true time function and after a transition region a formula becomes valid that corresponds to a transfer of cations by ambipolar diffusion. If the scale layer reaches the thickness of the surface stratum and exceeds it, then the surface stratum is detached from the metal and moves, without changing its thickness, forward with the oxide/oxygen boundary. Since the space charge of the surface stratum is not effective in the interval phase, the internal phase is also free of appreciable electric fields. The surface stratum shields the internal phase, so to speak. Thus, if the scale layer has become appreciably thicker than l, the transfer of the interstitial cations can occur only by diffusion and a new -- of course also parabolic -- time function with smaller rate constants and a different temperature dependence of the rate constants is valid.

Since the thickness of the surface stratum is, according to equation V, proportional to V_D and consequently inversely proportional to the concentration of the quasi-free electrons in the internal phase n_H, this break in the curve should lie at the minimum thickness of the surface layer the greater n_H is. Accordingly, the shift to the other time function must occur earlier with Zn-Al alloys as with Zn-Li alloys. No experimental evidence in this direction is yet available.

With the oxidation of zirconium and titanium, Gylbransen and coworker (19) found a deviation from the parabolic tarnish function with small oxide layer thickness that is analogous to the phenomena discussed above concerning the findings with zinc.

Discussion of the Findings of Moore and Lee

As already mentioned, Moore and Lee (12) found a parabolic tarnish function for the oxidation of zinc and simultaneously an oxygen pressure dependence of the oxidation rate constants that was incompatible with the Wagner Oxidation Theory (see Figures 5 and 6). However, these counterstatements are cleared up if it is kept in mind that the ZnO scales studies by Moore and Lee had a thickness of only 100-1,200 angstroms. In the case of these thin scales, the transfer of zinc ions through the ZnO layer is caused principally by electric fields. As pointed out above, however, the field strength in the surface stratum at the ZnO/O_2 phase boundary is a function of the surface concentration of the chemisorbed oxygen and thereby a function of the oxygen pressure itself. Since, however, in the case of the Moore-Lee studies the ZnO layer is identical with the surface stratum ($\xi < 1$), equations XIII and XIV are valid; i.e., thereby the findings of Moore and Lee which were noteworthy at first become reasonable.

To check the oxygen pressure dependence of the rate constants, we plotted the rate constants calculated by Moore and Lee from their measurements against $\log p_{O_2}$. Figure 7 shows the straight lines obtained. As is known, the experimental data will be described satisfactorily by equation XIV. On the basis of our graph, the Langmuir function introduced by Moore and Lee for time-determining adsorption appears to us to be of slight value.

The measurements of Moore and Lee may be clearly interpreted, on the other hand, as we have shown in explanations given above. It is, therefore, not to be assumed that in this case the active adsorption of the oxygen on the ZnO is itself rate-determining for the oxidation of the zinc. Rather it is the transfer of cations through the surface stratum, which here is identical with the scale layer, to the oxide/oxygen boundary which is considered as the slowest process since a phase boundary reaction as the slowest reaction must give a linear time function. Of course, the transfer rate depends on the diffusion potentials and thereby the oxygen pressure, so that the simultaneous occurrence of an oxygen pressure dependence of the reaction rate and a parabolic time function is compatible.

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